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High-temperature stability of thermoelectric $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films

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An enhanced thermal stability in thermoelectric $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films up to 550 °C in an oxygen rich environment was demonstrated by high-temperature electrical and X-ray diffraction measurements. In contrast to generally performed heating in helium gas, it is shown that an oxygen/helium mixture provides sufficient thermal contact, while preventing the previously disregarded formation of oxygen vacancies. Combining thermal cycling with electrical measurements proves to be a powerful tool to study the real intrinsic thermoelectric behaviour of oxide thin films at elevated temperatures. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4917275>]

Thermoelectric energy conversion is currently gaining an increased interest, because of the potential to recover waste heat into electrical energy. The efficiency of the thermoelectric generation process is determined by the electronic and thermal properties of the thermoelectric materials involved. Improvement of the performance of these thermoelectric materials forms therefore the main challenge to enhance the overall conversion efficiency. Furthermore, due to the presence of extensive waste heat at elevated temperatures in many application areas, high chemical and structural stability of thermoelectric materials at high temperatures is an important requirement.

Ceramic oxide materials are promising candidates for high-temperature applications due to their high chemical and structural stability. Among those complex oxides, the layered cobaltates exhibit the required combination of low electrical resistivity and high Seebeck coefficient, leading to values of the dimensionless figure of merit (ZT) of 1.2–2.7 for $\text{Ca}_3\text{Co}_4\text{O}_9$ single crystals.¹ High temperature studies on pressed, sintered $\text{Ca}_3\text{Co}_4\text{O}_9$ powders have demonstrated that the thermoelectric performance increases with temperature leading to a maximum ZT value of 0.25 for undoped samples and 0.6 for doped samples.² For these bulk materials, the high-temperature stability has been studied by thermal cycling, thermogravimetric analysis, and annealing in different atmospheres.^{2–4}

The study of $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films is an interesting route for exploring enhanced phonon scattering at interfaces, which is expected to result in a suppression of the thermal conductivity. Although studies on $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films have been previously reported,^{5–11} detailed thermoelectric characterization at elevated temperatures has not been shown. Therefore, important information on the thermal stability of such thermoelectric thin films has remained unknown. Here, we report the first, detailed high-temperature study of $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films, focusing on the thermal stability as well as the obtainable thermoelectric properties at elevated temperatures. Due to the enhanced surface to volume ratio, the reactivity of thin films is increased compared to bulk,

which will be determined by systematic thermal cycling in different gas environments. We demonstrate that an oxygen-rich atmosphere is crucial to obtain enhanced thermal stability of the $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films, in strong contrast to a helium atmosphere which is more generally used. Thermally stable $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films were achieved up to 550 °C exhibiting a maximum thermoelectric power factor of $5.2 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$, which is a significant enhancement compared to undoped bulk samples for which a maximum power factor of $3.6 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$ is observed.² These results support the implementation of cobaltate thin films as a route for high-temperature thermoelectric applications.

The $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films were grown by pulsed laser deposition, using a KrF excimer laser with a wavelength of 248 nm (Lambda-Physik LPX 210), a laser fluence of 4 J/cm^2 , a spotsize of 1.1 mm^2 , and a repetition rate of 1 Hz. During deposition, an oxygen pressure of 0.01 mbar and a substrate temperature of 750 °C were used, resulting in $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films with the highest crystallinity. After deposition, the thin films were slowly cooled down to room temperature in 1 atm of oxygen at a rate of 10 °C/min to optimize the oxidation level. As substrate material, (001) oriented single crystals of Al_2O_3 and $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.7}$ (LSAT) were used, which were annealed beforehand at 1050 °C for, respectively, 1 h and 10 h to obtain a smooth surface with predominantly unit-cell-height steps.¹² Hexagonal Al_2O_3 was chosen because of the good structural match with the hexagonal $\text{Ca}_3\text{Co}_4\text{O}_9$ in-plane crystal structure, whereas LSAT was used because of the recent observation of significant enhancement of the thermoelectric properties in Na_xCoO_2 thin films.¹²

To study the high-temperature structural properties, temperature dependent X-Ray diffraction (XRD) measurements were performed in air, using a Bruker D8 and a Panalytical XPert Pro MRD diffractometer, equipped with an Anton Paar domed hot stage. High-temperature measurements of the in-plane electrical resistivity and Seebeck coefficient were performed using a Linseis LSR3-1100 system. Using the sealed environment of the closed furnace, the measurements were performed in an atmosphere of 1.1 bar in which oxygen and helium gases could be mixed. Either pure helium or a oxygen/helium mixture, with 100 mbar oxygen, was

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introduced to ensure sufficient thermal contacts inside the system during the measurements. To demonstrate that adding 100 mbar of oxygen results in a sufficient partial oxygen pressure to ensure sample stability, pure oxygen gas was also used during resistivity measurements.

Single-phase $\text{Ca}_3\text{Co}_4\text{O}_9$ films with a thickness of 60 nm were deposited on Al_2O_3 and LSAT substrates with a preferred (001) oriented growth (Fig. 1(a)). Much stronger diffraction peaks are observed for thin films on Al_2O_3 , see inset of Fig. 1(a), due to the good in-plane match between both structures. Furthermore, $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films deposited on Al_2O_3 were found to be grown epitaxially, as shown by the phi-scans of the (104) and (112) diffraction peaks of, respectively, the substrate and the thin film in Fig. 1(b). From the relative positions of the substrate and film peaks, it is concluded that the a-axis of the rocksalt interlayers of the $\text{Ca}_3\text{Co}_4\text{O}_9$ is parallel to the a-axis of the Al_2O_3 , resulting in 12 peaks because of the three symmetrically comparable stacking options. No epitaxial relationship could be determined for films grown on LSAT, matching the reduced out-of-plane XRD intensity in Fig. 1(a). These $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films exhibit room temperature resistivities of 6 m Ω cm and 26 m Ω cm, and Seebeck coefficients of 133 $\mu\text{V/K}$ and 141 $\mu\text{V/K}$, for growth on, respectively, Al_2O_3 and LSAT

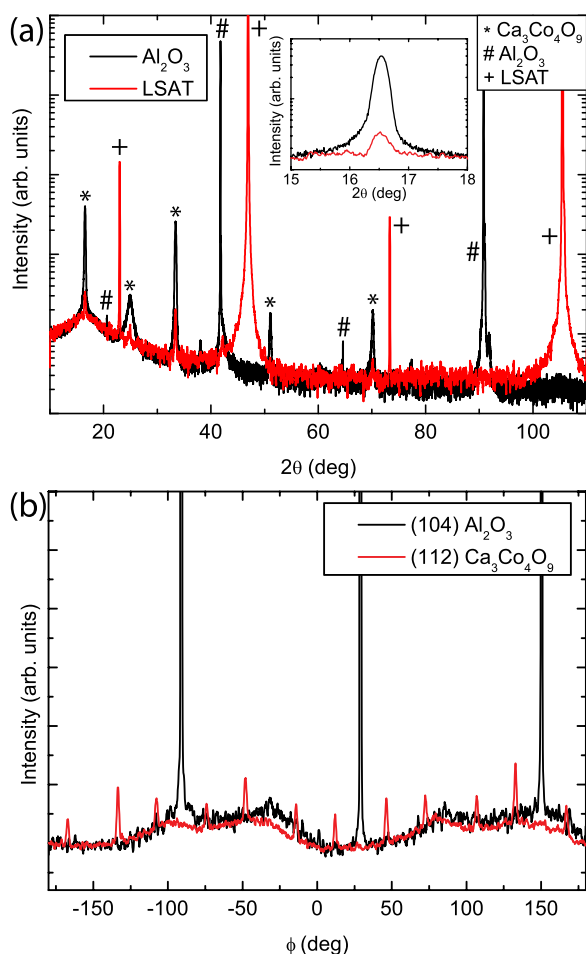


FIG. 1. XRD measurements of $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films deposited on Al_2O_3 and LSAT substrates. (a) $2\theta/\omega$ scan, showing only (001) peaks of the deposited $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films. The inset shows a zoom of the (002) $\text{Ca}_3\text{Co}_4\text{O}_9$ diffraction peak. (b) ϕ scan of the (104) and (112) peak of, respectively, the substrate and the thin film, demonstrating the epitaxial growth of $\text{Ca}_3\text{Co}_4\text{O}_9$.

substrates. The resulting thermoelectric power factors of $2.9 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$ for Al_2O_3 and $7.6 \times 10^{-5} \text{ W m}^{-1} \text{ K}^{-2}$ for LSAT agree well with the level of crystallinity for both cases. Similar thermoelectric properties have also been determined for thicker $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films in the range of 60–300 nm.¹³

The high-temperature stability of the $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films on Al_2O_3 substrates will be studied further in detail as they exhibit the most promising thermoelectric properties as well as the best crystallinity, which enables the characterisation of small structural changes at elevated temperatures. Using air as a background gas, temperature dependent $2\theta/\omega$ measurements were done around the (002) $\text{Ca}_3\text{Co}_4\text{O}_9$ diffraction peak, as it is the strongest diffraction peak for these thin films (see Fig. 1). The peak intensity and the c-axis lattice parameter were determined as a function of temperature, as shown in Fig. 2. The peak intensity is initially increasing, as also observed for the intensity of the substrate peaks, which is most likely caused by the XRD setup with the domed hot stage. Interestingly, a sharp decrease of the peak intensity is observed above a temperature of 750 °C. This sharp decrease is an indication of decomposition of the $\text{Ca}_3\text{Co}_4\text{O}_9$ film, which is confirmed by the absence of any $\text{Ca}_3\text{Co}_4\text{O}_9$ diffraction peaks at room temperature after these high-temperature measurements. For the temperature dependent c-axis lattice parameter, a linear increase is observed between room temperature and 750 °C, as shown in Fig. 2. The observed linear increase is caused by a thermal expansion of $1.8 \times 10^{-5} \text{ K}^{-1}$, in good agreement with the previous observations.¹⁴

The thermal stability and high-temperature thermoelectric properties are studied in detail by electrical resistivity and Seebeck measurements in a sequence of heating cycles. For each heating cycle, the temperature is swept from room temperature to a maximum temperature and back before increasing the maximum temperature in the next cycle. Using this measurement procedure, the data obtained during heating and cooling are compared to confirm that the sample has not changed during the measurement procedure. Figures 3(a) and 3(b) show measurements performed with helium as a background gas, which is the standard measurement gas because of its high thermal conductivity. As can clearly be seen in the resistivity measurements, the values obtained

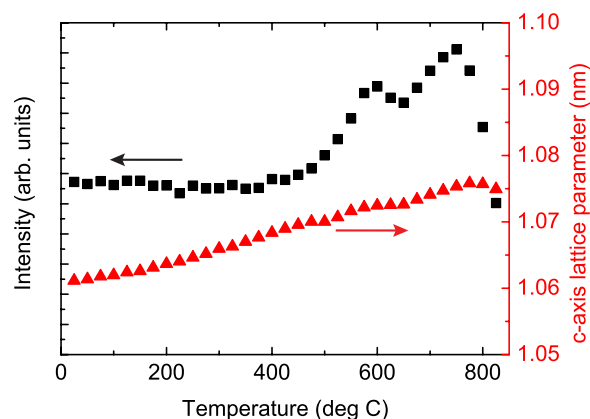


FIG. 2. High-temperature XRD measurements of a $\text{Ca}_3\text{Co}_4\text{O}_9$ thin film on Al_2O_3 substrate, showing the peak intensity of the (002) $\text{Ca}_3\text{Co}_4\text{O}_9$ diffraction peak and the c-axis lattice parameter.

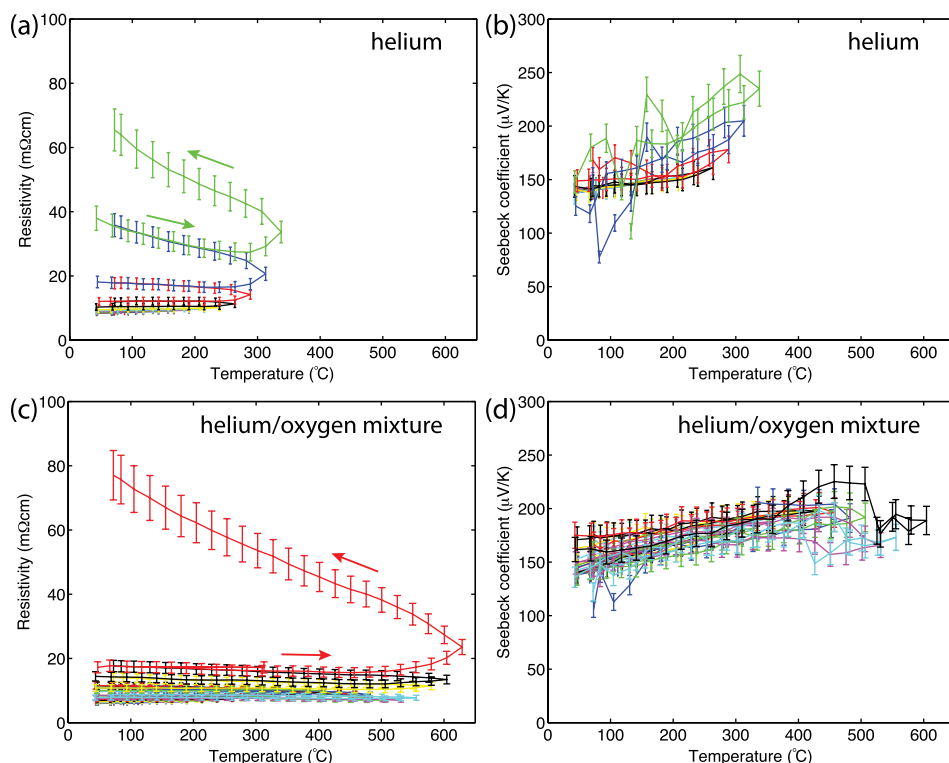


FIG. 3. High-temperature resistivity and Seebeck coefficient measurements with 1.1 bar helium ((a) and (b)) and oxygen/helium mixture ((c) and (d)) as background gas. For each heating cycle, the temperature is swept from room temperature to a maximum temperature and back before increasing the maximum temperature in the next cycle. Values are measured during heating as well as during cooling to determine the thermal stability.

during the heating and cooling procedures already significantly differ when the sample is only heated to approximately 300 °C. These observed changes indicate that these thin films are not stable when heated above 300 °C in helium gas and the obtained values are not the intrinsic values of these thin films. For the Seebeck coefficient, no clear differences are observed during heating and cooling, even though a relatively strong increase of the Seebeck coefficient as a function of temperature is observed. The observed poor thermal stability is most likely caused by the formation of oxygen vacancies at elevated temperatures in these oxide materials due to the use of helium as a background gas during these measurements.

To study the influence of the oxygen partial pressure on the thermal stability of these $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films, similar measurements were performed in a oxygen/helium gas mixture with 100 mbar of oxygen. This mixture still provides sufficient thermal contact to establish the required temperature gradient for the Seebeck coefficient measurements, which is not possible in pure oxygen or air. The results of these measurements are shown in Figs. 3(c) and 3(d). Compared to the measurements in helium, a significant improvement of the high-temperature stability is obtained when the samples are measured in a mixture of oxygen and helium. Up to a temperature of approximately 550 °C, the resistivity during heating and cooling overlaps, within the error margin of the measurements. When measured to even higher temperatures, a similar degradation, leading to an increase of the resistivity, is observed as in the thin films measured in helium. The Seebeck coefficient does not show a clear effect of the sample degradation, and the curves obtained from heating and cooling are relatively similar. Although small changes are observed, these are caused by variations in thermal and electrical contact to the samples, as confirmed by additional measurements at room temperature in a custom-built setup

after thermal cycling. These observations match those of the previous reports that the resistivity is much more sensitive to the background gas during thermal treatments⁴ than the Seebeck coefficient in bulk $\text{Ca}_3\text{Co}_4\text{O}_9$. This could be explained by a non-homogeneous sample degradation, starting at the sample surface. For these thin films, the surface to volume ratio is significantly larger than for bulk samples, leading to a significant change of the resistivity, as the volume of the conducting phase is considerably changing when a surface layer is formed. At the same time, this will not have such a pronounced influence on the Seebeck coefficient, because these measurements are not dependent on the volume of the conducting film and will not change if sufficient thermal and electrical contact is made with the thermoelectric phase.

The observed increase of the Seebeck coefficient at high temperatures is similar to the reports² of bulk $\text{Ca}_3\text{Co}_4\text{O}_9$, although the absolute Seebeck coefficient values from 140 $\mu\text{V/K}$ to 220 $\mu\text{V/K}$ in the temperature range of 25–550 °C are significantly higher than previously reported.² The electrical resistivity is relatively constant with temperature, in contrast to the previous reports of bulk $\text{Ca}_3\text{Co}_4\text{O}_9$ where a maximum is observed² around 150 °C. Thin films of $\text{Ca}_3\text{Co}_4\text{O}_9$ exhibit thermal stability up to temperatures of 550 °C at which an electrical resistivity and a Seebeck coefficient of 7.1 m Ω cm and 192 $\mu\text{V/K}$ have been determined. These values result in a thermoelectric power factor of $5.2 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$, which is a significant improvement compared to similarly undoped bulk samples for which a value of $3.0 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-2}$ is obtained at the same temperature range.² These results clearly demonstrate the high thermoelectric performance of $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films at elevated temperatures.

By comparing the high-temperature XRD measurements with the resistivity measurements, it is concluded that electronic measurements provide a more sensitive tool to study

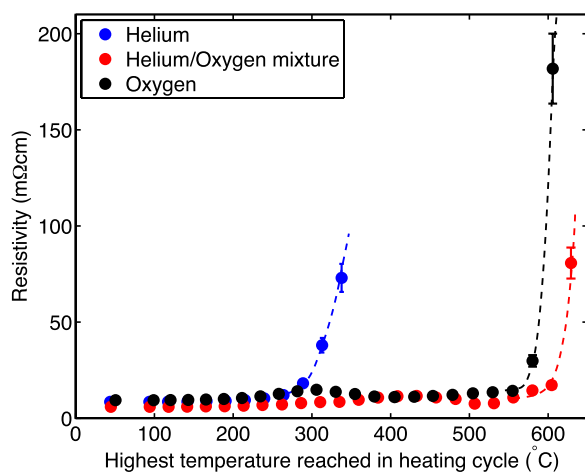


FIG. 4. Resistivity measurements of $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films at room temperature, after heating cycles in either helium, a helium/oxygen mixture, or pure oxygen to the maximum temperature shown on the horizontal axis. The dashed lines are a guide to the eye.

high-temperature stability of thin films. When only the XRD measurements are used, the samples seem to be stable up to 750 °C, whereas the electronic properties already show an irreversible change in behaviour above 550 °C. To further investigate this difference, the room temperature resistivity values after each heating cycle to a specific temperature are shown in Fig. 4. Three samples were heated in either helium, a helium/oxygen mixture or pure oxygen. Because the measurements of samples heated in a helium/oxygen mixture show a comparable trend to samples heated in pure oxygen, it is concluded that the used mixture provides a sufficient partial oxygen pressure to reveal the intrinsic sample stability. These room temperature values after heating confirm the significant difference in stability between measurements in helium and measurements with a sufficient partial oxygen pressure.

Based on these results, it is expected that the absence of oxygen when measured in helium results in the formation of oxygen vacancies, and thereby changes the carrier density and the carrier mobility. This is confirmed by Hall measurements at room temperature, from which the carrier density was obtained using a single band model. Before thermal cycling, a carrier density of $4 \times 10^{20} \text{ cm}^{-3}$ was obtained, in good agreement with the previous reports,¹⁵ which reduces to $1\text{--}2 \times 10^{20} \text{ cm}^{-3}$ after thermal cycling up to 350 °C. Furthermore, a reduction in carrier mobility by a factor of 4 was also caused by the formation of defects, oxygen vacancies, in the thin film. Interestingly, a strong directional anisotropy of the electronic transport was observed in the thin

film after thermal cycling, suggesting the inhomogeneous formation of oxygen vacancies.

A combination of high-temperature electrical measurements with high-temperature XRD measurements was performed to determine the thermal stability of epitaxial $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films on Al_2O_3 substrates up to a temperature of approximately 550 °C in an oxygen-rich environment. Similar thermal stability was also determined for textured $\text{Ca}_3\text{Co}_4\text{O}_9$ thin films on LSAT substrates.¹³ Accurate analysis of thermal stability can only be obtained by systematic thermal cycling and performing electrical measurements during heating as well as cooling of the samples, as the transport properties of these layered cobaltates provide a much more sensitive probe to the small changes in the structural properties. The lack of such systematic study in the previous studies on temperature dependent analysis of thermoelectric oxide materials has prevented the characterisation of the real intrinsic material properties and only reflect the behaviour of a changing system with additional oxygen vacancies or minor impurity phases. The presented method to use thermal cycling in combination with electrical measurements in different atmospheres is a powerful tool to study the intrinsic thermoelectric behaviour of oxide thin films.

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¹³See supplementary material at <http://dx.doi.org/10.1063/1.4917275> for experimental results on thickness dependence as well as thermal stability of textured films.

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